Exact Kohn-Sham exchange kernel for insulators and its long-wavelength behavior

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We present an exact expression for the frequency-dependent Kohn-Sham exact-exchange (EXX) kernel for periodic insulators, which can be employed for the calculation of electronic response properties within time-dependent (TD) density-functional theory. It is shown that the EXX kernel has a long-wavelength divergence behavior of the exact full exchange-correlation kernel and thus rectifies one serious shortcoming of the adiabatic local-density approximation and generalized-gradient approximations kernels. A comparison between the TDEXX and the GW-approximation-Bethe-Salpeter-equation approach is also made.

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I. INTRODUCTION

Time-dependent density-functional theory (TDDFT)[1,2] is an attractive first-principles formalism for the calculation of electronic response properties. Thanks to its simplicity, applications to quantum wells[3] and atoms[4] have appeared long before its formal justification,[5] and currently its use is ubiquitous in a wide range of *ab initio* computations. A crucial ingredient of successful TDDFT applications is the approximation to the *dynamic* exchange-correlation kernel,

$$F_{\rm xc}(\mathbf{r},\mathbf{r}';t-t') \equiv \frac{\delta v_{\rm xc}(\mathbf{r};t)}{\delta n(\mathbf{r}';t')}, \quad (1)$$

which together with the Hartree kernel[6] $F_{\rm H}(\mathbf{r},\mathbf{r}') = w_C(\mathbf{r},\mathbf{r}') \equiv 1/|\mathbf{r}-\mathbf{r}'|$ completely determines the two-particle interaction effects. For $F_{\rm xc}$, the adiabatic local-density approximation (LDA) kernel,

$$F_{\rm xc}^{LDA}(\mathbf{r},\mathbf{r}';t-t') = \delta(t-t')\delta(\mathbf{r}-\mathbf{r}')\frac{dv_{\rm xc}^{LDA}[n(\mathbf{r})]}{dn(\mathbf{r})}, \quad (2)$$

has been almost exclusively adopted in practical calculations. However, the scope of the LDA kernel has been rather limited for infinite periodic solids due to its deficiencies, and in particular its incorrect non-divergent long-wavelength behavior for insulators has been emphasized as a primary defect in recent years.[7,8,9] This shortcoming of the LDA kernel shows up, e.g., in its incapability of describing excitonic effects in absorption spectra of solids. The semilocal generalized gradient approximations (GGA) kernel does not improve over the LDA one in this case, and the task of developing a more accurate approximate exchange-correlation kernel remains as a challenging task for the TDDFT study of solids.

Indeed deficiencies of the LDA and GGA appear already at the level of the *static* exchange-correlation energy functional $E_{xc}[n]$ and the exchange-correlation potential $v_{\rm xc}(\mathbf{r}) \equiv \delta E_{\rm xc}[n]/\delta n(\mathbf{r})$. For instance, the LDA and GGA $E_{xc}[n]$ inherently fails to describe the quasi-two-dimensional electron gas due to their (semi)local nature.[10] For $v_{\rm xc}$ and the corresponding Kohn-Sham (KS) eigenvalues, the LDA and GGA $v_{\rm xc}$ incorrectly decays exponentially rather than as $-1/r$ for localized systems, and consequently their highest occupied orbital energies are too high and unoccupied orbital energies do not exhibit Rydberg series. For solids, the LDA band gaps are too small and this behavior is again not corrected by the GGA. In fact, even the exact KS gap does not equal the experimental band gap but differs by the discontinuity of the exchange-correlation potential.[11] However, recent theoretical and numerical studies suggested that the KS equation for N electrons corresponds to the Dyson equation where the reference ground state is chosen with $N-1$ electrons,[12] and accordingly unoccupied orbitals in the KS calculations should give a good description of excitations of the N-electron system with fixed particle number. This is in accordance with the perturbation theory along the adiabatic connection[13] which finds that differences of KS eigenvalues represent the leading term in the expansion of excitation energies.

In this regard, recent development of the KS exact-exchange (EXX) method, which treats the exchange-correlation energy functional exactly in leading order in the electron-electron interaction, provides an interesting opportunity. Self-interaction-free, nonlocal EXX schemes give not only realistic exchange potentials and KS eigenvalue spectra for molecules[14,15,16,17,18] but also band structures of semiconductors in good agreement with experiments.[19,20] We have recently shown that the EXX orbitals and eigenvalues at the one-particle level without any previously applied post-DFT modification such as the quasiparticle shift[21] indeed give a very good description of the absorption spectrum of semiconductors with the exception of excitonic features resulting from two-particle interactions, and argued that it is another evidence of the above-described picture of "KS quasiparticles".[22]

In view of the encouraging performance of the EXX method, we present in this work an exact expression of the EXX kernel $F_{\rm x}^{EXX}$ for periodic insulators which can be employed for calculations of electronic linear response properties within TDDFT. It will be shown that the EXX kernel, unlike the LDA and GGA kernels, exhibits a long-wavelength behavior of the exact $F_{\rm xc}$ which is particularly important for the study of electronic excitations in

infinite solids. This behavior of the EXX kernel has been previously claimed by Goshez *et al.* based on a plausibility argument,[8] and here we explicitly prove this using our exact formula.

II. LONG-WAVELENGTH BEHAVIOR OF THE EXCHANGE-CORRELATION KERNEL FOR INSULATORS

We first establish the definitions and notations of various quantities of interest and derive the long-wavelength behavior of the exact $F_{\rm xc}$.[8] The full linear density response matrix χ describes the response of the first-order (number) density change δn for the given bare dynamic perturbation $\delta v_{\rm ext}$,

$$\delta n(\mathbf{G},\mathbf{q};\omega) = \sum_{\mathbf{G}'} \chi(\mathbf{G},\mathbf{G}',\mathbf{q},\omega)\,\delta v_{\rm ext}(\mathbf{G}',\mathbf{q};\omega). \quad (3)$$

We chose to work in the reciprocal space and the frequency domain, e.g., $\chi(\mathbf{G},\mathbf{G}',\mathbf{q};\omega)$ is a matrix in the reciprocal-space lattice vectors $\mathbf{G}$ and $\mathbf{G}'$ for the given wave-vector $\mathbf{q}$ and frequency ω. Analysis of the $q\to 0$ behavior of the "head" ($\mathbf{G}=\mathbf{G}'=0$), "wing" ($\mathbf{G}=0$ and $\mathbf{G}'\neq 0$ or vice versa), and "body" ($\mathbf{G}\neq 0$ and $\mathbf{G}'\neq 0$) elements of χ and other related matrices appearing below is an important discussion point throughout the paper. From now on, we will adopt the matrix notation and $\mathbf{G}$ dependence will be assumed unless explicitly stated otherwise. Within TDDFT, δn is expressed in terms of the dynamic linear response matrix χ_0 and the first-order change of the effective KS potential $\delta v_{\rm KS}$,

$$\delta n(\mathbf{q};\omega) = \chi_0(\mathbf{q};\omega)\,\delta v_{\rm KS}(\mathbf{q};\omega), \quad (4)$$

where $\delta v_{\rm KS}$ is composed of the external perturbation $\delta v_{\rm ext}$ and the resulting change in the Hartree potential $\delta v_{\rm H}$ and the exchange-correlation potential $\delta v_{\rm xc}$,

$$\begin{aligned}\delta v_{\rm KS}(\mathbf{q};\omega) &= \delta v_{\rm ext}(\mathbf{q};\omega) + \delta v_{\rm H}(\mathbf{q};\omega) + \delta v_{\rm xc}(\mathbf{q};\omega)\\ &= \delta v_{\rm ext}(\mathbf{q};\omega) + \big[F_{\rm H}(\mathbf{q}) + F_{\rm xc}(\mathbf{q};\omega)\big]\,\delta n(\mathbf{q};\omega),\end{aligned} \quad (5)$$

with $F_{\rm H}(\mathbf{G},\mathbf{G}',\mathbf{q}) = \delta_{\mathbf{G},\mathbf{G}'} 4\pi/|\mathbf{q}+\mathbf{G}|^2$. Then, from Eqs. (3), (4), and (5), one obtains

$$\chi_0^{-1}(\mathbf{q};\omega) = \chi^{-1}(\mathbf{q};\omega) + F_{\rm H}(\mathbf{q}) + F_{\rm xc}(\mathbf{q};\omega), \quad (6)$$

which shows that χ is completely determined once χ_0 and $F_{\rm xc}$ are given.

For further consideration of the $q\to 0$ behavior of $F_{\rm xc}$, it is convenient to introduce the "proper" part of χ, $\widetilde{\chi}$, defined through[8,23]

$$\delta n(\mathbf{q};\omega) = \widetilde{\chi}(\mathbf{q};\omega)\,\delta v_{\rm TC}(\mathbf{q};\omega), \quad (7)$$

where $\delta v_{\rm TC}$ is the change of the test-charge potential,

$$\delta v_{\rm TC}(\mathbf{q};\omega) \equiv \delta v_{\rm ext}(\mathbf{q};\omega) + F_{\rm H}(\mathbf{q})\,\delta n(\mathbf{q};\omega), \quad (8)$$

and thus relates with the full response matrix χ as

$$\widetilde{\chi}^{-1}(\mathbf{q};\omega) = \chi^{-1}(\mathbf{q};\omega) + F_{\rm H}(\mathbf{q}), \quad (9)$$

or with the KS response matrix χ_0 as

$$\chi_0^{-1}(\mathbf{q};\omega) = \widetilde{\chi}^{-1}(\mathbf{q};\omega) + F_{\rm xc}(\mathbf{q};\omega). \quad (10)$$

The linear response matrix of the *non-interacting KS* system χ_0 and the proper part of that of the *real interacting* system $\widetilde{\chi}$ are known to have the following similar $q\to 0$ behavior[23,24] (assuming that both the KS system and the real system are insulating[8]):

$$\chi_0 = \begin{bmatrix} q^2\,\chi_0^{00} & q\,\chi_0^{01} \\ q\,\chi_0^{10} & \chi_0^{11}\end{bmatrix};\ \widetilde{\chi} = \begin{bmatrix} q^2\,\widetilde{\chi}^{00} & q\,\widetilde{\chi}^{01} \\ q\,\widetilde{\chi}^{10} & \widetilde{\chi}^{11}\end{bmatrix}, \quad (11)$$

where we used the notation that ξ^{00}, $\xi^{01/10}$, and ξ^{11} denote the head of a matrix ξ divided by q^2, its wings divided by q, and its body, respectively. The quantities χ_0^{00}, χ_0^{10}, χ_0^{01}, and χ_0^{11} as well as $\widetilde{\chi}^{00}$, $\widetilde{\chi}^{10}$, $\widetilde{\chi}^{01}$, and $\widetilde{\chi}^{11}$ all consist of a leading $\mathbf{q}$-*independent* term and contributions of higher order in q which vanish in the limit $q\to 0$. Then, from Eqs. (10) and (11), one can deduce that the head and wings of $F_{\rm xc}$ have the following divergent $q\to 0$ behavior[8] (assuming that there exists no fortuitous cancellation between χ_0^{-1} and $\widetilde{\chi}^{-1}$),

$$F_{\rm xc} = \begin{bmatrix} F_{\rm xc}^{00}/q^2 & F_{\rm xc}^{01}/q \\ F_{\rm xc}^{10}/q & F_{\rm xc}^{11}\end{bmatrix}, \quad (12)$$

In Eq.(12), $F_{\rm xc}^{00}$, $F_{\rm xc}^{10}$, $F_{\rm xc}^{01}$, and $F_{\rm xc}^{11}$ again contain a leading $\mathbf{q}$-*independent* term and contributions of higher order in q which vanish for $q\to 0$. The head and wings of adiabatic LDA and GGA kernels, on the other hand, are independent of q and thus are incorrectly non-divergent for $q\to 0$:

$$F_{\rm xc}^{LDA/GGA} = \begin{bmatrix} F_{\rm xc}^{LDA/GGA,00} & F_{\rm xc}^{LDA/GGA,01} \\ F_{\rm xc}^{LDA/GGA,10} & F_{\rm xc}^{LDA/GGA,11}\end{bmatrix}. \quad (13)$$

This defect is a serious problem not only from a theoretical viewpoint but also for practical purposes because the head and wings of the exchange-correlation kernel can affect the the macroscopic dielectric function in leading order.[8] For example, it has been recently shown that they play a crucial role for the proper treatment of excitonic effects in the calculation of optical spectra.[9]

III. EXACT-EXCHANGE KERNEL AND ITS LONG-WAVELENGTH BEHAVIOR FOR INSULATORS

Deficiencies of the LDA and GGA kernels discussed above represent a major problem from the theoretical and calculational point of view which could not be overcome so far. To ameliorate the situation we propose to adopt the EXX kernel. An exact expression of the EXX kernel

has been previously derived by one of us for localized systems for the case of real-valued orbitals.[25] For periodic solids, we need to generalize this expression to complex orbitals and have to consider the dependence on wave vectors $\mathbf{k}$ and $\mathbf{q}$. This leads to

$$F_{\rm x}^{EXX}(\mathbf{G},\mathbf{G}',\mathbf{q};\omega) = \sum_{\mathbf{G}_1,\mathbf{G}_2} \chi_0^{-1}(\mathbf{G},\mathbf{G}_1,\mathbf{q};\omega) \times H_{\rm x}(\mathbf{G}_1,\mathbf{G}_2,\mathbf{q};\omega)\,\chi_0^{-1}(\mathbf{G}_2,\mathbf{G}',\mathbf{q};\omega), \tag{14}$$

where the EXX kernel "core" $H_{\rm x}$ is composed of the following contributions (We assume that $\delta v_{\rm ext}(\mathbf{q};\omega)$ and other quantities have the time-dependence $e^{-i\omega t}e^{\delta t}$, where $\delta \to 0^+$ is a convergence factor.):

$$H_{\rm x}^1(\mathbf{G},\mathbf{G}',\mathbf{q};\omega) \equiv -\frac{2}{\Omega}\sum_{as\mathbf{k}}\sum_{bt\mathbf{k}'}\Big[\frac{\langle a\mathbf{k}|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|s\mathbf{k}+\mathbf{q}\rangle\langle s\mathbf{k}+\mathbf{q};b\mathbf{k}'|\widehat{w}_C|t\mathbf{k}'+\mathbf{q};a\mathbf{k}\rangle\langle t\mathbf{k}'+\mathbf{q}|e^{i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}}|b\mathbf{k}'\rangle}{(\epsilon_{a\mathbf{k}}-\epsilon_{s\mathbf{k}+\mathbf{q}}+\omega+i\delta)(\epsilon_{b\mathbf{k}'}-\epsilon_{t\mathbf{k}'+\mathbf{q}}+\omega+i\delta)} + \frac{\langle s\mathbf{k}|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|a\mathbf{k}+\mathbf{q}\rangle\langle a\mathbf{k}+\mathbf{q};t\mathbf{k}'|\widehat{w}_C|b\mathbf{k}'+\mathbf{q};s\mathbf{k}\rangle\langle b\mathbf{k}'+\mathbf{q}|e^{i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}}|t\mathbf{k}'\rangle}{(\epsilon_{a\mathbf{k}}-\epsilon_{s\mathbf{k}+\mathbf{q}}-\omega-i\delta)(\epsilon_{b\mathbf{k}'}-\epsilon_{t\mathbf{k}'+\mathbf{q}}-\omega-i\delta)}\Big], \tag{15}$$

$$H_{\rm x}^2(\mathbf{G},\mathbf{G}',\mathbf{q};\omega) \equiv -\frac{2}{\Omega}\sum_{as\mathbf{k}}\sum_{bt\mathbf{k}'}\Big[\frac{\langle a\mathbf{k}|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|s\mathbf{k}+\mathbf{q}\rangle\langle s\mathbf{k}+\mathbf{q};t\mathbf{k}'|\widehat{w}_C|b\mathbf{k}'+\mathbf{q};a\mathbf{k}\rangle\langle b\mathbf{k}'+\mathbf{q}|e^{i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}}|t\mathbf{k}'\rangle}{(\epsilon_{a\mathbf{k}}-\epsilon_{s\mathbf{k}+\mathbf{q}}+\omega+i\delta)(\epsilon_{b\mathbf{k}'}-\epsilon_{t\mathbf{k}'+\mathbf{q}}-\omega-i\delta)} + \frac{\langle s\mathbf{k}|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|a\mathbf{k}+\mathbf{q}\rangle\langle a\mathbf{k}+\mathbf{q};b\mathbf{k}'|\widehat{w}_C|t\mathbf{k}'+\mathbf{q};s\mathbf{k}\rangle\langle t\mathbf{k}'+\mathbf{q}|e^{i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}}|b\mathbf{k}'\rangle}{(\epsilon_{a\mathbf{k}}-\epsilon_{s\mathbf{k}+\mathbf{q}}-\omega-i\delta)(\epsilon_{b\mathbf{k}'}-\epsilon_{t\mathbf{k}'+\mathbf{q}}+\omega+i\delta)}\Big], \tag{16}$$

$$\begin{aligned} H_{\rm x}^3(\mathbf{G},\mathbf{G}',\mathbf{q};\omega) \equiv & -\frac{2}{\Omega}\sum_{abs\mathbf{k}}\Big[\frac{\langle a\mathbf{k}|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|s\mathbf{k}+\mathbf{q}\rangle\langle b\mathbf{k}|\widehat{\Sigma}_x-\widehat{v}_x|a\mathbf{k}\rangle\langle s\mathbf{k}+\mathbf{q}|e^{i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}}|b\mathbf{k}\rangle}{(\epsilon_{a\mathbf{k}}-\epsilon_{s\mathbf{k}+\mathbf{q}}+\omega+i\delta)(\epsilon_{b\mathbf{k}}-\epsilon_{s\mathbf{k}+\mathbf{q}}+\omega+i\delta)} \\ & + \frac{\langle s\mathbf{k}|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|a\mathbf{k}+\mathbf{q}\rangle\langle a\mathbf{k}+\mathbf{q}|\widehat{\Sigma}_x-\widehat{v}_x|b\mathbf{k}+\mathbf{q}\rangle\langle b\mathbf{k}+\mathbf{q}|e^{i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}}|s\mathbf{k}\rangle}{(\epsilon_{a\mathbf{k}}-\epsilon_{s\mathbf{k}+\mathbf{q}}-\omega-i\delta)(\epsilon_{b\mathbf{k}}-\epsilon_{s\mathbf{k}+\mathbf{q}}-\omega-i\delta)}\Big] \\ & +\frac{2}{\Omega}\sum_{ast\mathbf{k}}\Big[\frac{\langle a\mathbf{k}|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|s\mathbf{k}+\mathbf{q}\rangle\langle s\mathbf{k}+\mathbf{q}|\widehat{\Sigma}_x-\widehat{v}_x|t\mathbf{k}+\mathbf{q}\rangle\langle t\mathbf{k}+\mathbf{q}|e^{i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}}|a\mathbf{k}\rangle}{(\epsilon_{a\mathbf{k}}-\epsilon_{s\mathbf{k}+\mathbf{q}}+\omega+i\delta)(\epsilon_{a\mathbf{k}}-\epsilon_{t\mathbf{k}+\mathbf{q}}+\omega+i\delta)} \\ & + \frac{\langle s\mathbf{k}|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|a\mathbf{k}+\mathbf{q}\rangle\langle t\mathbf{k}|\widehat{\Sigma}_x-\widehat{v}_x|s\mathbf{k}\rangle\langle a\mathbf{k}+\mathbf{q}|e^{i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}}|t\mathbf{k}\rangle}{(\epsilon_{a\mathbf{k}}-\epsilon_{s\mathbf{k}+\mathbf{q}}-\omega-i\delta)(\epsilon_{a\mathbf{k}}-\epsilon_{t\mathbf{k}+\mathbf{q}}-\omega-i\delta)}\Big], \end{aligned} \tag{17}$$

and

$$
\begin{aligned}
H_{\rm x}^4(\mathbf{G},\mathbf{G}',\mathbf{q};\omega) \equiv -\frac{2}{\Omega}\sum_{abs\mathbf{k}}\Big[&\frac{\langle b\mathbf{k}|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|s\mathbf{k}+\mathbf{q}\rangle\langle s\mathbf{k}+\mathbf{q}|\widehat{\Sigma}_x-\widehat{v}_x|a\mathbf{k}+\mathbf{q}\rangle\langle a\mathbf{k}+\mathbf{q}|e^{i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}}|b\mathbf{k}\rangle}{(\epsilon_{b\mathbf{k}}-\epsilon_{s\mathbf{k}+\mathbf{q}}+\omega+i\delta)(\epsilon_{a\mathbf{k}}-\epsilon_{s\mathbf{k}+\mathbf{q}})}\\
&+\frac{\langle b\mathbf{k}|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|a\mathbf{k}+\mathbf{q}\rangle\langle a\mathbf{k}+\mathbf{q}|\widehat{\Sigma}_x-\widehat{v}_x|s\mathbf{k}+\mathbf{q}\rangle\langle s\mathbf{k}+\mathbf{q}|e^{i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}}|b\mathbf{k}\rangle}{(\epsilon_{a\mathbf{k}}-\epsilon_{s\mathbf{k}+\mathbf{q}})(\epsilon_{b\mathbf{k}}-\epsilon_{s\mathbf{k}+\mathbf{q}}+\omega+i\delta)}\\
&+\frac{\langle s\mathbf{k}|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|b\mathbf{k}+\mathbf{q}\rangle\langle a\mathbf{k}|\widehat{\Sigma}_x-\widehat{v}_x|s\mathbf{k}\rangle\langle b\mathbf{k}+\mathbf{q}|e^{i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}}|a\mathbf{k}\rangle}{(\epsilon_{b\mathbf{k}}-\epsilon_{s\mathbf{k}+\mathbf{q}}-\omega-i\delta)(\epsilon_{a\mathbf{k}}-\epsilon_{s\mathbf{k}+\mathbf{q}})}\\
&+\frac{\langle a\mathbf{k}|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|b\mathbf{k}+\mathbf{q}\rangle\langle s\mathbf{k}|\widehat{\Sigma}_x-\widehat{v}_x|a\mathbf{k}\rangle\langle b\mathbf{k}+\mathbf{q}|e^{i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}}|s\mathbf{k}\rangle}{(\epsilon_{a\mathbf{k}}-\epsilon_{s\mathbf{k}+\mathbf{q}})(\epsilon_{b\mathbf{k}}-\epsilon_{s\mathbf{k}+\mathbf{q}}-\omega-i\delta)}\Big]\\
+\frac{2}{\Omega}\sum_{ast\mathbf{k}}\Big[&\frac{\langle a\mathbf{k}|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|t\mathbf{k}+\mathbf{q}\rangle\langle s\mathbf{k}|\widehat{\Sigma}_x-\widehat{v}_x|a\mathbf{k}\rangle\langle t\mathbf{k}+\mathbf{q}|e^{i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}}|s\mathbf{k}\rangle}{(\epsilon_{a\mathbf{k}}-\epsilon_{t\mathbf{k}+\mathbf{q}}+\omega+i\delta)(\epsilon_{a\mathbf{k}}-\epsilon_{s\mathbf{k}+\mathbf{q}})}\\
&+\frac{\langle s\mathbf{k}|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|t\mathbf{k}+\mathbf{q}\rangle\langle a\mathbf{k}|\widehat{\Sigma}_x-\widehat{v}_x|s\mathbf{k}\rangle\langle t\mathbf{k}+\mathbf{q}|e^{i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}}|a\mathbf{k}\rangle}{(\epsilon_{a\mathbf{k}}-\epsilon_{s\mathbf{k}+\mathbf{q}})(\epsilon_{a\mathbf{k}}-\epsilon_{t\mathbf{k}+\mathbf{q}}+\omega+i\delta)}\\
&+\frac{\langle t\mathbf{k}|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|a\mathbf{k}+\mathbf{q}\rangle\langle a\mathbf{k}+\mathbf{q}|\widehat{\Sigma}_x-\widehat{v}_x|s\mathbf{k}+\mathbf{q}\rangle\langle s\mathbf{k}+\mathbf{q}|e^{i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}}|t\mathbf{k}\rangle}{(\epsilon_{a\mathbf{k}}-\epsilon_{t\mathbf{k}+\mathbf{q}}-\omega-i\delta)(\epsilon_{a\mathbf{k}}-\epsilon_{s\mathbf{k}+\mathbf{q}})}\\
&+\frac{\langle t\mathbf{k}|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|s\mathbf{k}+\mathbf{q}\rangle\langle s\mathbf{k}+\mathbf{q}|\widehat{\Sigma}_x-\widehat{v}_x|a\mathbf{k}+\mathbf{q}\rangle\langle a\mathbf{k}+\mathbf{q}|e^{i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}}|t\mathbf{k}\rangle}{(\epsilon_{a\mathbf{k}}-\epsilon_{s\mathbf{k}+\mathbf{q}})(\epsilon_{a\mathbf{k}}-\epsilon_{t\mathbf{k}+\mathbf{q}}-\omega-i\delta)}\Big].
\end{aligned}
\tag{18}
$$

In Eqs.(15)-(18), 2 is the spin factor, Ω is the crystal volume, $\{a,b\}$ are valence bands, $\{s,t\}$ are conduction bands, $\langle i\mathbf{k}+\mathbf{q};j\mathbf{k}'|\widehat{w}_C|l\mathbf{k}'+\mathbf{q};m\mathbf{k}\rangle$ are four-index integrals defined as

$$
\begin{aligned}
\langle i\mathbf{k}+\mathbf{q};j\mathbf{k}'|\widehat{w}_C|l\mathbf{k}'+\mathbf{q};m\mathbf{k}\rangle &\equiv \int d\mathbf{r}\int d\mathbf{r}'\ \frac{\phi^*_{i\mathbf{k}+\mathbf{q}}(\mathbf{r})\phi^*_{j\mathbf{k}'}(\mathbf{r}')\phi_{l\mathbf{k}'+\mathbf{q}}(\mathbf{r})\phi_{m\mathbf{k}}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\\
&=\frac{4\pi}{\Omega}\sum_{\mathbf{G}}\frac{\langle i\mathbf{k}+\mathbf{q}|e^{i(\mathbf{G}+\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}}|l\mathbf{k}'+\mathbf{q}\rangle\langle j\mathbf{k}'|e^{-i(\mathbf{G}+\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}'}|m\mathbf{k}\rangle}{|\mathbf{G}+\mathbf{k}-\mathbf{k}'|^2},
\end{aligned}
\tag{19}
$$

$\widehat{\Sigma}_x$ is a nonlocal orbital-dependent exchange operator of the form of the Hartree-Fock exchange operator but constructed with the KS orbitals ϕ_a,

$$
\begin{aligned}
\langle i\mathbf{k}+\mathbf{q}|\widehat{\Sigma}_x|j\mathbf{k}+\mathbf{q}\rangle &\equiv -\int d\mathbf{r}\int d\mathbf{r}'\phi^*_{i\mathbf{k}+\mathbf{q}}(\mathbf{r})\sum_{a\mathbf{k}'}\frac{\phi_{a\mathbf{k}'}(\mathbf{r})\phi^*_{a\mathbf{k}'}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\phi_{j\mathbf{k}+\mathbf{q}}(\mathbf{r}')\\
&=-\sum_{a\mathbf{k}'}\langle i\mathbf{k}+\mathbf{q};a\mathbf{k}'|\widehat{w}_C|a\mathbf{k}';j\mathbf{k}+\mathbf{q}\rangle\\
&=-\frac{4\pi}{\Omega}\sum_{a\mathbf{k}'\mathbf{G}}\frac{\langle i\mathbf{k}+\mathbf{q}|e^{i(\mathbf{G}+\mathbf{k}-\mathbf{k}'+\mathbf{q})\cdot\mathbf{r}}|a\mathbf{k}'\rangle\langle a\mathbf{k}'|e^{-i(\mathbf{G}+\mathbf{k}-\mathbf{k}'+\mathbf{q})\cdot\mathbf{r}'}|j\mathbf{k}+\mathbf{q}\rangle}{|\mathbf{G}+\mathbf{k}-\mathbf{k}'+\mathbf{q}|^2},
\end{aligned}
\tag{20}
$$

and $\widehat{v}_x$ is generated by the local multiplicative EXX KS potential $v_x(\mathbf{r})$.

Compared with the LDA (or GGA) kernel which is (semi)local in real space and frequency-independent [Eq. (2)], which results in a reciprocal-representation independent of $\mathbf{q}$ and ω, $F_{\rm xc}^{LDA/GGA}(\mathbf{G},\mathbf{G}',\mathbf{q};\omega) = F_{\rm xc}^{LDA/GGA}(\mathbf{G}-\mathbf{G}')$, $F_{\rm x}^{EXX}$ is fully nonlocal in real space and depends explicitly on the frequency. We now show that $F_{\rm x}^{EXX}$ has a $q\to 0$ behavior as the exact $F_{\rm xc}$. By expanding orbitals $\phi_{j\mathbf{k}+\mathbf{q}}$ in terms of the orbitals $\phi_{i\mathbf{k}}$ employing perturbation theory,[23,24]

$$
\phi_{j\mathbf{k}+\mathbf{q}} = \phi_{j\mathbf{k}} + \sum_{i\neq i}\phi_{i\mathbf{k}}\frac{\mathbf{q}\cdot\langle i\mathbf{k}|\mathbf{p}|j\mathbf{k}\rangle}{\epsilon_{i\mathbf{k}}-\epsilon_{j\mathbf{k}}},
\tag{21}
$$

we express various matrix elements of Eqs.(15)−(18) in power series in $\mathbf{q}$ and keep only the leading non-vanishing terms. Then, one can first observe that $\langle i\mathbf{k};j\mathbf{k}'|l\mathbf{k}';m\mathbf{k}\rangle$ and $\langle i\mathbf{k}|\widehat{\Sigma}_x-\widehat{v}_x|j\mathbf{k}\rangle$ are the leading order terms in q of $\langle i\mathbf{k}+\mathbf{q};j\mathbf{k}'|l\mathbf{k}'+\mathbf{q};m\mathbf{k}\rangle$ and $\langle i\mathbf{k}+\mathbf{q}|\widehat{\Sigma}_x-\widehat{v}_x|j\mathbf{k}+\mathbf{q}\rangle$ and that consequently the $\mathbf{q}$-dependence can be ignored for $q\to 0$ in the inner matrix elements of Eqs. (15)−(18).

One might notice that the inner matrix elements $\langle i\mathbf{0}+\mathbf{q};j\mathbf{0}|i\mathbf{0}+\mathbf{q};j\mathbf{0}\rangle$ in $H_{\rm x}^1$ contain a singular contribution, the term with $\mathbf{G}=0$ in Eq. (19). However, the same singularities with the opposite sign arise in the matrix elements $\langle i\mathbf{k}+\mathbf{q}|\widehat{\Sigma}_x|j\mathbf{k}+\mathbf{q}\rangle$ of the first two contributions of $H_{\rm x}^3$, the terms with $\mathbf{G}=0$ and $\mathbf{k}'=\mathbf{k}+\mathbf{q}$ in Eq. (20). So the Coulomb singularities in the inner matrix elements of $H_{\rm x}^1$ and $H_{\rm x}^3$ exactly cancel.

Unlike in the case of inner matrix elements, for the other outer matrix elements $\langle i\mathbf{k}|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|j\mathbf{k}+\mathbf{q}\rangle$ or $\langle i\mathbf{k}+\mathbf{q}|e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}}|j\mathbf{k}\rangle$ with $i\neq j$, $\mathbf{q}$-dependent contributions appear in leading order in q for $\mathbf{G}=0$ or $\mathbf{G}'=0$[24], e.g.,

$$\lim_{q\to 0}\langle i\mathbf{k}|e^{-i\mathbf{q}\cdot\mathbf{r}}|j\mathbf{k}+\mathbf{q}\rangle=\mathbf{q}\cdot\frac{\langle i\mathbf{k}|\mathbf{p}|j\mathbf{k}\rangle}{\epsilon_{i\mathbf{k}}-\epsilon_{j\mathbf{k}}}. \qquad (22)$$

In $H_{\rm x}^4$, however, matrix elements $\langle i\mathbf{k}|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|i\mathbf{k}+\mathbf{q}\rangle$ and $\langle i\mathbf{k}+\mathbf{q}|e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}}|i\mathbf{k}\rangle$ are present, for which a leading order term independent of q occurs for $\mathbf{G}=0$ or $\mathbf{G}'=0$. However, contributions of such type in the first sum of $H_{\rm x}^4$ are cancelled by corresponding contributions in the second sum.

Due to the cancellations of singularities, $H_{\rm x}$ itself is well-defined, and the $q\to 0$ behavior of $H_{\rm x}$ can be deduced as

$$H_{\rm x}=\begin{bmatrix} q^2\,H_{\rm x}^{00} & q\,H_{\rm x}^{01} \\ q\,H_{\rm x}^{10} & H_{\rm x}^{11}\end{bmatrix} \qquad (23)$$

with $H_{\rm x}^{00}$, $H_{\rm x}^{10}$, $H_{\rm x}^{01}$, and $H_{\rm x}^{11}$ containing a leading order term independent of q. Consequently, using Eqs. (11), (14), and (23), we conclude that $F_{\rm x}^{EXX}$ has the $q\to 0$ behavior of the exact $F_{\rm xc}$,

$$F_{\rm x}^{EXX}=\begin{bmatrix} F_{\rm x}^{EXX,00}/q^2 & F_{\rm x}^{EXX,01}/q \\ F_{\rm x}^{EXX,10}/q & F_{\rm x}^{EXX,11}\end{bmatrix} \qquad (24)$$

with $F_{\rm x}^{00}$, $F_{\rm x}^{10}$, $F_{\rm x}^{01}$, and $F_{\rm x}^{11}$, again containing a q-independent leading order term.

IV. DISCUSSION AND CONCLUSIONS

Now we analyze the physical meaning of $H_{\rm x}$ and relate it with the GW approximation (GWA)-Bethe-Salpeter equation (BSE) approach,[26] which represents at the moment the most successful first-principles computational scheme of electronic excitations in solids. We start by rewriting Eq. (10) as $\widetilde{\chi}=(1-\chi_0F_{\rm xc})^{-1}\chi_0$. By first expanding $(1-\chi_0F_{\rm xc})^{-1}$ in a power series into $1+\chi_0F_{\rm xc}+\chi_0F_{\rm xc}\chi_0F_{\rm xc}+...$, next taking only the first two leading terms of this expansion, and finally neglecting correlation contributions, $(1-\chi_0F_{\rm xc})^{-1}\approx 1+\chi_0F_{\rm x}^{EXX}$, we obtain $\widetilde{\chi}\approx\chi_0+\chi_0F_{\rm x}^{EXX}\chi_0$. Thus, identifying $\chi_0F_{\rm x}^{EXX}\chi_0$ as $H_{\rm x}$ [See Eq. (14)], we can interpret $H_{\rm x}$ as the first order correction to χ_0 in $\widetilde{\chi}$,

$$\widetilde{\chi}(\mathbf{q};\omega)\approx\chi_0(\mathbf{q};\omega)+H_{\rm x}(\mathbf{q};\omega). \qquad (25)$$

Indeed, $H_{\rm x}$ has been recently shown in the many-body diagrammatic language as the first-order self-energy and vertex corrections to the irreducible polarizability $\widetilde{\chi}$.[27]

The expression of the full $H_{\rm x}$ is admittedly quite complicated. However, we point out that a simplified picture of the important underlying physical processes within TDEXX can be extracted by noting that only the first term of $H_{\rm x}^1$ ($H_{\rm x}^{1-r}$) and the first and third terms of $H_{\rm x}^3$ ($H_{\rm x}^{3-r}$) are dominant contributions at resonant ω. This is schematically depicted in Fig. 1.

Note that the above situation is similar to the one that occurs in the solution of the BSE where the Tamm-Dancoff approximation is invoked.[26] In fact, with the EXX kernel, we can easily make a connection between the TDDFT and the GWA-BSE approach. Consider calculation of the full response function[9] or excitation energies[27,28] with TDEXX and GWA-BSE. Replacing the bare Coulomb interaction with the screened Coulomb interaction, the resonant terms of $H_{\rm x}^3$ effectively shift the EXX eigenvalue spectrum toward that of the GWA, while the resonant terms in $H_{\rm x}^1$ are the counterparts of those occurring in the BSE in the Tamm-Dancoff approximation.

In the above comparison, it is interesting to observe that while the GWA and BSE have a clear hierarchy as the theory of independent quasiparticle excitations[29] and electron-hole excitations, terms related to both excitation effects appear within the DFT formulation at the time-dependent level and the distinction between one- and two-particle excitations is accordingly rather arbitrary. We should also mention that the mapping between TDEXX and GWA-BSE is not exact because the $H_{\rm x}^4$ terms do not have counterparts in the GWA-BSE. These differences may indicate the inherently different nature of TDDFT and the GWA-BSE approach.

In summary, we derived the expression of the EXX kernel for insulators and showed that it has a long-wavelength behavior as the exact $F_{\rm xc}$ unlike the LDA and GGA kernels. The common conception that DFT is not suitable for the study of electronic excitations of solids was mainly derived by adopting *qualitatively* incorrect LDA and GGA potentials and kernels and the difficulty of going beyond them. Coupled with the already available EXX potential, we expect the numerical realization of the EXX kernel will open up a new window of opportunity for the first-principles study of electronic excitations in solids.[30]

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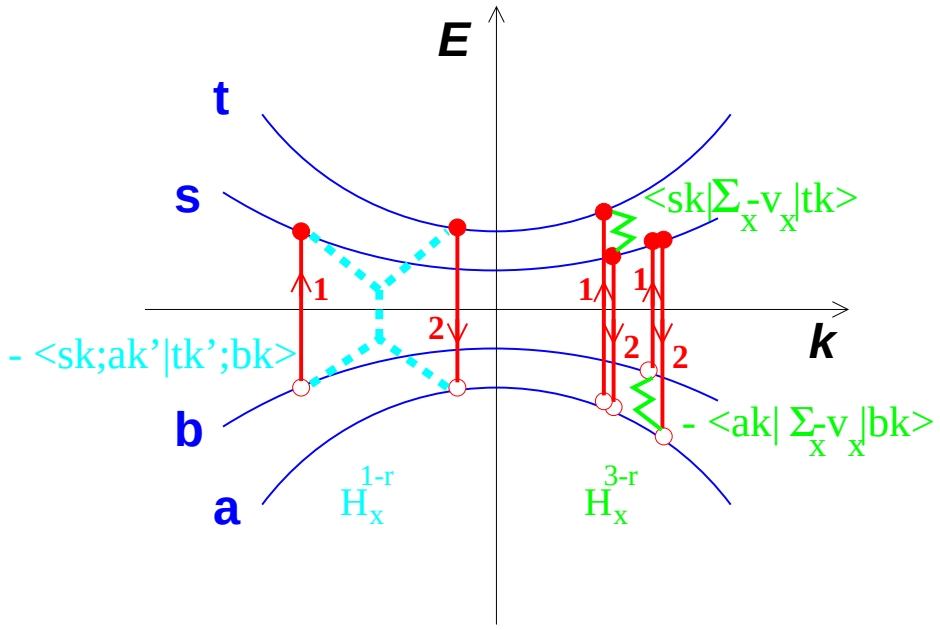

FIG. 1: Schematic description of the resonant contributions to $H_{\rm x}$ ($H_{\rm x}^{1-r}$ and $H_{\rm x}^{3-r}$). Arrow 1 and 2 represent $\langle s\mathbf{k}+\mathbf{q}|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|a\mathbf{k}\rangle$ and $\langle a\mathbf{k}|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|s\mathbf{k}+\mathbf{q}\rangle$. They involve the *time-sequential* coupling of an electron excitation from valence $\{a,b\}$ to conduction $\{s,t\}$ bands (hole $\rightarrow$ electron pair) and a relaxation from conduction to valence bands (electron $\rightarrow$ hole pair).